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Hydrothermal conversion of lignin: A review

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ABSTRACT

Lignin is a carbon-rich renewable source owning aromatic structure units, which is an important constituent in biomass. Hydrothermal conversion of lignin is widely studied as a promising method to produce not only bioenergy but also value-added useful chemicals. Fuel gas, aromatic aldehydes and phenolic products can be obtained from lignin hydrothermal gasification, wet oxidation and hydrothermal liquefaction, respectively. This article discusses and compares the three methods of lignin hydrothermal conversion, including their process parameters, possible conversion routes, catalysts, application of products. Effects of hot-compressed organic solvent–water mixture solution on conversion of lignin and effects of lignin in biomass hydrothermal conversion are commented. Wet oxidation of lignin is an efficient mean of recovering value-added aromatic aldehydes, especially vanillin. Hydrothermal liquefaction of lignin is a promising way of recovering phenolics-rich bio-oils. Both aromatic aldehyde and phenolic compound are important chemical intermediates. There are strict requirements of process conditions and relative high costs to get fuel gas from direct hydrothermal gasification of lignin. However, further studies on improving gasification of lignin seem necessary in order to get fuel gas from hydrothermal gasification of the whole biomass.

Contents

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1. Introduction

Lignin is the only renewable source of aromatics, which consists of three basic structural units, p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These structural units are connected by ether and C–C bonds, as shown in Fig. 1 [1]. Based on its phenolic functionalities and properties, lignin offers possibilities for higher value-added renewable products applications. Moreover, lignin constitutes up to 30% of the weight and 40% of the fuel value of biomass it can be used to increase fuel production [2]. Lignin is usually a co-product of paper and pulping, as well as lignocellulosic bioethanol industries, while the predominant pulping process is likely to produce the most available source of lignin [3]. However, it is important to illustrate that different biomass source and pretreatment recovering method would result in change of lignin content and composition. Usually, the herbaceous plants have the lowest content of lignin, whereas softwoods have the highest lignin content [4]. The herbaceous lignin is a polymer owning all these three basic structural units, softwood lignin is mainly composed of coniferyl alcohol unit, while hardwood lignin consists of mainly coniferyl alcohol and sinapyl alcohol units. On the other hand, alcell™ organosolv lignin has higher phenolic hydroxyl content and a lower number of carboxyl groups than the soda lignins [5]. Moreover, a strongest lignin modification was observed in the kraft lignin recovered from the alkaline pulping liquor, most of the modified lignin during pulping was released to the cooking liquor [6]. Baptista et al. found that the pulping procedure influenced the lignin structure, namely the lateral chain degradation, the content of hydroxyl groups and condensed lignin units [7]. Lawther et al. found that through alkaline nitrobenzene oxidation, a slightly high guaiacyl content in the original wheat straw, and relatively high syringyl content in alkali treated wheat straw [8]. Therefore, it is hard to get a uniform exploitation model for all kinds of lignins. However, lignin is an important composition in biomass, it is necessary to study the properties of lignin in order to use the whole biomass. Moreover, lignin is an abundant, sustainable phenolic polymer and carbon-neutral material, and it should be a good source of valuable chemicals if it could be broken into smaller molecular units.

Recently, most lignin is directly burned to generate energy, which has many disadvantages. For example, some pretreatment such as drying before combustion process is required; the storage of the burning product heat is difficult, the heat should be used immediately; moreover, the emission of burning gas and ash would result in environmental problems. Many interesting and valuable works on degradation of lignin for biofuels and valuable compounds have been studied, these works include hydrothermal conversion, pyrolysis [9–11], enzymatic degradation [12], photo-catalysed degradation [13], electrochemical degradation [14], ionic liquids degradation [15], microwave irradiation oxidation [16], etc. Based on the lignin degradation methods, some reviews of conversion of lignin are published: Zakzeski et al. [17] give an overview of catalytic valorization of lignin. Bietti and Lanzalunga [18] give a review on photo- and radiation degradation of lignin model compounds. Hofrichter [19] gives a critical review of lignin conversion by manganese peroxidase. Less in detail, review [20] by Pandey and Kim covers all types of thermochemical methods. Some lignin related reviews [21,22] on pyrolysis and biodegradation of lignin are also reported. Hydrothermal conversion of lignin is a promising method, which has been extensively studied. This article focuses on the hydrothermal conditions, and then a critical review on lignin decomposition into renewable chemicals is provided.

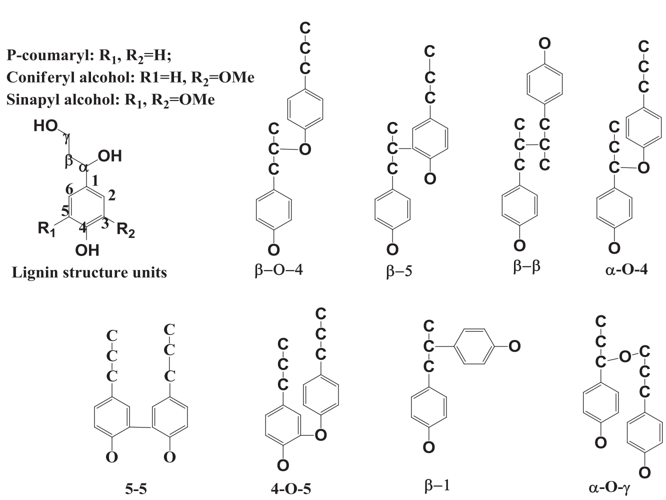


Fig. 1. Lignin structure units and the linkages.

2. Hydrothermal conditions

Hydrothermal technologies are broadly defined as chemical and physical transformations in high-temperature, high-pressure liquid or supercritical water (SCW) [23]. SCW is the water in the state over the critical point of 374.2 °C and 22.1 MPa. Several researchers have given positive evaluation on hydrothermal conversion technology. Bobleter reported hydrothermal degradation is an effective technology to decompose polymer derived from plants [24], while Garrote et al. thought hydrothermal processes are environment-friendly technologies that can be conceived as a first step for the chemical utilization of lignocelluloses [25]. Compared with other lignin degradation methods, the hydrothermal treatment has some excellent properties. (1) There is unnecessary of predrying, it can be an absolute cost advantage in treating the papermaking wastewater lignins, (2) N and S are the common elements in lignin, nitrogen oxides and sulfur oxides would be released in some degradation methods, while these oxides produced in hydrothermal conditions would be dissolved in water, further treatment is not needed, (3) in hydrothermal conditions, water can be used as a hydrogen source [26], which is very important in the gasification of lignin, even biomass for hydrogen production, and (4) the existence of hydrolysis reaction would result in a relative low operating conditions, such as the required hydrothermal temperature is usually lower than other biomass thermo-chemical method including pyrolysis and steam gasification [27–29]. When the hydrothermal conditions reach the SCW states, some more advantages would be shown. The effects of water for organic chemical reactions in SCW are versatile, performing as reactant, catalyst, desolvation of transition, density inhomogeneities [30]. Water behaves like many organic solvents in that lignin derived low molecular weight organic compounds and gases enjoy high solubility in or complete miscibility with SCW, and there is no interphase mass transport process to hinder reaction rates. Higher dispersivity and better heat transfer characteristic should be provided in the SCW than those in gas and

liquid. Therefore, compared with other hot water medium, SCW would accelerate and reinforce decomposition degree of lignin. Similar experimental result was reported that biomass was more easily decomposed in SCW than that in subcritical water [31]. The hydrothermal conversion of lignin in this review includes wet air oxidation, liquefaction, and gasification. Moreover, effects of hot-compressed organic solvent–water solution on conversion of lignin and effects of lignin in biomass hydrothermal conversion are discussed.

3. Wet oxidation of lignin

Wet oxidation (WO) is a thermal aqueous phase process in which organic and inorganic substances in aqueous solutions or suspensions are oxidized by oxidant at elevated temperatures and pressures [32]. The operating temperatures and pressures are ranging from 100 °C to 320 °C and from 0.5 MPa to 20 MPa, respectively [33]. Though some of WOs of lignin are studied as treatment of wastewaters [34,35], a few studies were focused on the oxidation of lignin for organic acids production, it was reported that 0.45 g/g-lignin and 0.20 g/g-lignin of organic acids were recovered from alkali lignin and organosolv lignin at different temperatures, respectively [36]. Most depolymerizations of lignins by WOs are used to produce aromatic aldehydes, e.g., vanillin, syringaldehyde, and p-hydroxy-benzaldehyde. These aldehydes have many applications, vanillin is especially widely used as a flavoring and fragrance ingredient in the food, cosmetic, and pharmaceutical industries. However, among these products, only vanillin is presently manufactured on an industrial scale, though the yield of vanillin is not high. Table 1 summarizes studies of wet oxidation of lignin for aromatic aldehydes production in the recent years.

3.1. Catalysts

Catalysts are often used to increase the yields of aldehydes in the lignin WO processes. Such catalysts are mainly composed of noble metals, transition metal salts, and perovskite-type compounds. Noble metals own great catalytic effects, more than 10–20 times of aromatic aldehydes could be produced with a palladium catalyst compared with those oxidation processes without catalyst [52]. Moreover, noble metals usually exist as solid particles, which are conducive to recovery and reuse. However, noble metals are not suitable for the economics of commercial applications because of their high cost. Compared with noble metals, transition metal salts are more interest to industry because of their low cost. Transition metal salts are usually water soluble so they always act as homogeneous catalyst. Heterogeneous effectiveness can result in higher catalytic activity, Cu^{2+} was found to be the most effective homogeneous catalyst [53], and cupric sulfates are being investigated widely because of their effectiveness. The order of homogeneous catalytic activity observed was $Cu^{2+} > Fe^{2+} > Mn^{2+} > Ce^{2+} > Bi^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > Ni^{2+}$ [53]. One of the problems affecting the use of homogeneous catalyst in industry is their difficulty in recovery. For the homogeneous catalyst $H_3PMo_{12}O_{40}$, approximately 40% of the $H_3PMo_{12}O_{40}$ was lost from the reaction medium up to the last run [46]. Furthermore, these homogeneous transition metal salts can result in secondary pollution during the emission of water. Lin' group [37–41] has done great contributions on perovskite-type oxide catalysts, they find these perovskite-type oxide

Table 1
Wet oxidation of lignin for aromatic aldehydes production.

Authors' reference	Raw materials	Temperature	Catalyst	Reactor	Yield of vanillin	Yield of syringaldehyde	Yield of p-hydroxy-benzaldehyde
Deng et al. [37–40]	Steam-exploded lignin from cornstalk	120 °C	$LaCoO_3$	Stainless-steel autoclave	4.55%^{m}	9.99%^{m}	2.23%^{m}
			$LaCo_{1-x}Cu_xO_3$ ($x=0$, 0.1, and 0.2)		5.30% ^{m}	12.8% ^{m}	2.88% ^{m}
			$LaFeO_3$		4.10% ^{m}	8.77% ^{m}	1.89% ^{m}
			$LaMnO_3$		4.321% ^{m}	9.326%^{m}	2.032%^{m}
Zhang et al. [41]	Pinus spp kraft lignin	120 °C	$LaFe_{1-x}Cu_xO_3$ ($x=0$, 0.1, 0.2)		4.56%^{m}	11.51%^{m}	2.49%^{m}
Sales et al. [42,43]	Lignin obtained from sugarcane bagasse	100/120/140 °C	Palladium supported on γ-alumina	Batch reactor, continuous reactor	1.87% (batch), 2.17% (continuous)	1.67% (batch), 3.83% (continuous)	
				Continuous regime	The best yield in aromatic aldehydes was of 12%		
Pinto et al. [44,45]	(Kraft, sulfite, organosolv) lignins and (hardwood, softwood) lignins	120 °C		Autoclave			
	Pinus spp. kraft lignin, lignoboost kraft lignin, organosolv beech lignin	120 °C		Autoclave	4.4%^{m}	2.5%^{m}	0.17%^{m}
Voitl et al. [46]	Kraft lignin	170 °C	$H_3PMo1_2O_{40}$	Autoclave	3.5 wt%		
Xiang et al. [47]	Lignin obtained from liriodendron tulipifera	160–180 °C	$CuSO_4$ and $FeCl_3$	Tubing bomb reactor	2.1–5.1%	1.6–9.8%	
Santos et al. [48]	Magnesium-based lignosulfonate	130–150 °C	$CuSO_4$	Stainless reactor	4.5%^{m}	16.1%^{m}	
Fargues et al. [49]	Pinus spp. Kraft lignin	110–154 °C	–	Autoclave	10.8%^{m}		
Araújo et al. [50]	Pinus spp kraft lignin	150 °C		Autoclave	3.5–7.6%		
Silva et al. [51]	Pinus spp. Westvaco lignin, Indulin AT Westvaco lignin,	119–141 °C		Batch reactor	2.8–10.8%		

^{m}: the max yield.

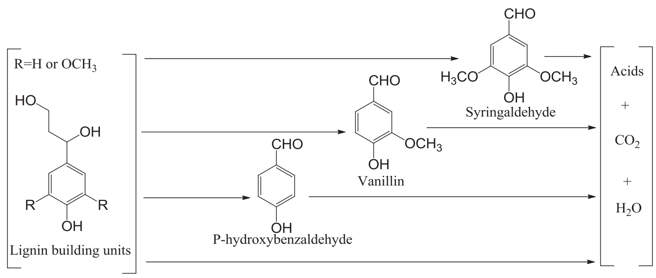


Fig. 2. Reaction scheme of wet oxidation of lignin.

catalysts exhibit high activity and stability in the catalytic WO of lignin. Compared with the transition metals, these perovskite-type oxides need a supernumerary production process by a sol–gel method.

3.2. Affecting conditions

As shown in Fig. 2, the lignin degradation for aldehydes production is a complex series/parallel reaction network. Vanillin, syringaldehyde, p-hydroxybenzaldehyde are intermediates of the lignin wet oxidation process, according to lignin's three structure units. These aldehydes can be obtained in appropriate conditions because the activation energies of these three aromatic aldehydes are much higher than that of lignin, and the lignin degradation was characterized for a faster reaction step, with an low activation energy (44.26 kJ/mol) [52]. However, these aldehydes can be subsequent oxidized into organic acids such as formic, lactic, syringic, vanillic, and p-hydroxybenzoic acids, or even CO_2 and H_2O as the end products. To improve the lignin degradation and avoid loss of the aldehydes by excessive oxidation, many scholars have studied the optimum operating conditions for various lignins [42,43,45,51,52]. Though Tarabanko et al. demonstrated that the rate of oxidation should be increased using more severe reaction conditions in order to enhance the selectivity of lignin oxidation to aromatic aldehydes [54]. Moderated partial pressures of oxygen, reaction times, and temperatures are the vitally necessary process parameters, because any of high temperature, high partial pressures of oxygen, and long reaction times would accelerate the unwished conversion of aromatic aldehydes. As shown in Table 1, the reaction temperatures are among 100–190 °C. Besides these, lignin molecular weight is a crucial parameter in vanillin production [50,55], lower molecular weight lignins could contain more amounts of precursors which are responsible for vanillin yield. It was reported vanillin yields with respect to the lignin mass ranging from 3.5% to 7.6% for the high and low-molecular weight lignins, respectively [50]. Lignin is an organic polymer with a structure that depends strongly on the source and the producing/recovering conditions. Lignin types are important for the three aldehydes' production, softwood lignin consists of mainly guaiacyl propane unit and a small quantity of hydroxyphenyl unit, which means vanillin would be the main products. All of the vanillin, syringaldehyde, and p-hydroxybenzaldehyde would be obtained from the herbaceous lignin, which owns all of the three basic units. More syringaldehyde would be obtained from hardwood lignin due to its high content of syringyl propane unit. pH value could affect both the conversion of lignin and aromatic aldehydes. Increasing the pH enhanced the lignin removal efficiency [34,35]. While at lower values of pH, the vanillin degraded at a considerable rate reducing its yield [50,51]. For strong alkaline conditions, there was a small vanillin degradation that increased sharply when pH was smaller than 11.5 [50]. So it is important to make special consideration to adjust the pH value when the goal is to produce vanillin from lignin oxidation. In a continuous reactor, oxygen mass transfer constant was a significant parameter, low oxygen mass transfer from gas to liquid phase limited the extent of vanillin production [56]. Continuous reactor is very important for industrial applications, it was reported that the fine aldehyde production process from batch to continuous operation presented a yield increase of approximately 15 times higher in 2 h of operation [42].

3.3. Separation

In the process of lignin oxidation to produce aromatic aldehydes, the reaction media contains other species such as unconverted lignin, salt of aromatic aldehydes, aromatic acids, acetovanillone, etc. The isolation of aromatic aldehydes from the oxidized solution is an important stage. Liquid–liquid extraction with suitable organic solvents (benzene or toluene) for recovery of vanillin from wet air oxidation of lignin has been conducted in industrial companies. Before the organic solvent extraction, acidification of the reactant medium is necessary to precipitate the unconverted lignin and other lignin derived high molecular weight compounds. Other separation methods including ultrafiltration membrane technique and ion-exchange technique have been studied by Rodrigues' group [51,57,58]. The ultrafiltration membrane technique has been evaluated to recover vanillin from kraft lignin oxidation. Ultrafiltration process can be used as an efficient way for the recovery of vanillin from kraft lignin oxidation product, with very high cleaning efficiency using sodium hydroxide solution [57]. And ion-exchange processed through the column filled with ion-exchanger in H^+ form was found a useful method for recovery vanillin [58]. Rodrigues' group has put up a purified vanillin recovering method using consecutive membrane, ion-exchange and crystallization processes [51]. However, application of the ultrafiltration membrane and ion-exchange require some limited conditions (such as moderate temperature, appropriate pH value and low suspension solids concentration). Moreover, the cost of ultrafiltration membrane and ion-exchange resin is somewhat high.

4. Hydrothermal gasification

Hydrothermal gasification of woody biomass has received great attention as a promising technology for conversion of biomass into gas. Moreover, black liquor gasification in SCW is reported bringing both environment and energy benefits [59–61]. When the moisture content is more than 30%, SCW gasification is more attractive than the conventional gasification method for biomass [62]. As an important component in biomass and a main organic component in black liquor, lignin gasification in hydrothermal conditions is abundantly studied. However, it was indicated that lignin cannot be gasified without the formation of solid products at low temperatures (250–400 °C) [63], which may be due to the existence of phenolic units that are stable in decomposition but easy for polymerization. Therefore, complete gasification of lignin is probably a key technology for achieving sustainable fuel sources from woody biomass and/or black liquor. While considering the costs of treating wastewater, SCW gasification can be competitive with biomethanation [64], which means that SCW gasification of lignin rich black liquor would be a promising method.

4.1. Products and separation

The gasification products mainly consist of CO_2, and fuel gases including H_2, CO, CO_2, CH_4, and even a little bit of C_2H_4, C_2H_6. These fuel gases have wide-ranging applications including the use in fuel cells, gas turbines, and synthesis gas. Separation seems necessary in order to get high-value utilization of mixed gases, there are two separation methods. (1) Isolation of CO_2 from the fuel gases, the object is to improve the calorific value of the fuel gases. These fuel gases may have abilities to a good substitute for town gas and/or liquefied petroleum gas and (2) purification of H_2 from product gas, the object is to get high-value H_2. H_2 has a great potential of

application in the future, especially the application through fuel cell. A high-pressure separator can be a valuable unit in lignin hydrothermal gasification system for H_2 production, in which the hydrogen is purified by dissolving CO_2 and other gases into the water phase. Besides water, 1-hexanol is an effective solvent for dissolving CO_2, and it was reported that using the weight amount of one-tenth of water, 1-hexanol can make higher or comparable hydrogen purity in the vapor phase and less hydrogen dissolved in the liquid phase [65]. In a simulation separation process of biomass SCW gasification products, hydrogen purities from 73 to 81% in mole fraction can be obtained with a high-pressure separator in appropriate operating conditions [66]. However, it is hard to separate H_2 from the CO, CH_4, C_2H_4, C_2H_6 only in a high-pressure separator [67], further treatments are necessary to get high-purity H_2 from the H_2 rich gases. The treatments can be membrane separation [68,69], pressure-swing adsorption [70], cryogenic separation [71], and hydrate method [72], or some regeneration methods. It was reported that high concentration (99%) hydrogen stream could be obtained from a solid regeneration system [73].

4.2. Affecting conditions

The biomass, including lignin, gasification in SCW is a complex process, which includes a group of successive reaction and competing intermediate reactions, including hydrolysis, polymerization, water–gas shift, hydrogenation, steam reforming, and methanation. These reactions are essential for a complete gasification, and these reactions are inevitably affected by temperature, pressure, reaction time, concentration, and catalysts. For example, high temperature is benefit to steam-reforming reaction and free-radical reactions [74,75]. Moreover, gasification reactions are usually endothermic, increased temperature would promote of the decomposition of lignin into gaseous species. While high pressure increases the amount of H^+ or OH^-, and therefore accelerates the hydrolysis; but high pressure is adverse to free-radical reaction and decomposition reaction. Temperature shows a most significant effect on noncatalytic SCW gasification of lignin. High temperature resulted in high hydrogen yield, high carbon efficiency and high gasification efficiency [74], and it was reported that high temperature of about 700 °C or higher was necessary for complete gasification of lignin [74]. Moreover, the water–gas shift reaction started at very high temperatures from 575 °C [76]. The similar results of carbon efficiency and gasification efficiency were shown in SCW gasification of black liquor, and maximum conversion to H_2, CO, CH_4, and C_2H_X was achieved at the highest temperature of 650 °C [59]. Moreover, higher reaction temperature resulted in increased hydrogen percentage of gaseous products [77]. While in a KOH catalytic gasification of lignin model compound pyrocatechol, the formation of methane at high temperature (600 °C) was kinetically inhibited [78]. In gasification of lignin at hydrothermal conditions from 15 to 27.5 MPa, increased pressure is benefit to high carbon efficiency and gasification efficiency, besides, higher pressure results in higher hydrogen and methane percents, but lower carbon dioxide percent in gas products [79]. Furthermore, higher pressure causes higher water density, while lignin decomposition rate increased with increasing the water-density [80,81], and one of the effects of water-density was that the first step (decomposition to low-molecular weight compounds) in the lignin gasification was enhanced by increasing the water density. And water density affected the reaction kinetics in catalytic SCW gasification of lignin, the yield of methane and carbon dioxide increased with increasing water density but then decreased and leveled out to constant values [82]. High concentration of lignin was not suitable for lignin gasification, higher concentration resulted in lower carbon efficiency, gasification efficiency and hydrogen yield [79], and an increase in black liquor feed concentration led to lower SCW gasification energy efficiency [59]. However, improving gasification effects of high concentration lignin is very important, which could benefit the gasification of high concentration of woody biomass. On the other hand, the lignin concentration in black liquor is very high, while gasification of black liquor without dilution would bring operation convenience and economic benefits. However, hydrolysis and hydrothermal reactions of organic molecules lead to a bunch of compounds, it was reported that it was difficult to obtain special compounds at high concentrations [83]. Considering the existing high temperature and pressure, and the requirement of reactor materials for higher temperature and pressure in hydrothermal conditions, further studies on high-performance selective catalysts which could improve the gasification of high concentration lignin seem necessary. Longer reaction time would make the gasification more completely and get more total gas yield. However, it was reported that shorter reaction time was in favor of hydrogen percentage of gaseous products in a metal catalytic SCW gasification of lignin [77]. While in a non-catalytic gasification of lignin, longer reaction times resulted in more yield of hydrogen [79]. Moreover, the yield of hydrogen from lignin was firstly increased and then decreased with increasing reaction times in an alkali catalytic SCW gasification [84]. These results indicate that in a hydrogen production from lignin SCW gasification without or with different kind of catalysts, the effects of reaction time would be variable. In a whole, too long reaction time would lead to undesirable conversion of fragments and unnecessary consumption of energy; too short reaction time causes insufficient decomposition of lignin. As a result, moderate reaction time should be explored for lignin gasification in various conditions.

4.3. Catalysts

In the absence of catalysts, CH_4 and CO_2 are always the major products from SCW gasification of lignin, and lower H_2 and CO yields are obtained [85]. Catalysts are necessary for high hydrogen yield production. There were mainly three categories of catalysts in lignin hydrothermal gasification, including alkali and alkali salt (NaOH, KOH, Na_2CO_3, CaO, $NaHCO_3$, etc.), metal, and a few of metal oxides, e. g., ZrO_2 [86].

For transition metal catalysts, such as Ni, Pt, Ru and Rh, most studies suppose that they improve the reaction by accelerating the steam reforming reaction, methanation reaction and cleavage of C–O and C–C and so on [87]. Resende and Savage found that all of the metals (nickel, iron, zinc, and zirconium wires, and ruthenium powder) tested produced H_2 from water when exposed to SCW gasification conditions with no biomass [88]. Ruthenium and its salts are well known catalysts. The gasification of lignin on a supported ruthenium catalysts proceeded in SCW through two steps [81]: (1) decomposition of lignin to low-molecular weight compounds and (2) gasification of the low-molecular weight compounds over metal catalysts. Effects of three ruthenium catalyst in lignin gasification in SCW were discussed, the order of activity was $Ru/C = Ru(NO)(NO_3)_3/C > RuCl_3/C$, the reason was that the size of ruthenium metal in $Ru(NO)(NO_3)_3/C$ was smaller than that in $RuCl_3/C$ [89].

Various noble metal catalysts were used to test the abilities for methane, carbon dioxide and hydrogen selectivities and yields in catalytic SCW gasification of lignin and its model compounds. The values for selectivity to methane were in the following order, ruthenium > rhodium > platinum > palladium > nickel [81]. The order of metal species for the organosolv-lignin gasification was following: ruthenium > rhodium > platinum > palladium > nickel; while the order of hydrogen production for gasification of organosolv-lignin was following: palladium > ruthenium > platinum > rhodium > nickel [77]. In the gasification of lignin model

compounds alkylphenols, the activity of the catalyst was in the order of Ru/ç-alumina > Ru/carbon, Rh/carbon > Pt/ç-alumina, Pd/carbon, and Pd/ç-alumina [90]. These results indicate that both the types of catalyst and lignin would influence the gasification yield and composition in the catalytic gasification conditions.

Catalytic stability of noble metal catalysts in lignin gasification is a problem pressed for solution. Deactivation of metal catalysts in lignin SCW gasification usually because of decrease of specific surface area and active sites poisoning. The decrease of specific surface area includes agglomeration of noble metal, deposit of lignin derived char, and the change in carrier's structure. The yield of total gas of lignin gasification was considerably dropped after the Ni/MgO catalyst was used three times, this was because of the agglomeration and deposit caused low specific surface area of Ni/MgO catalyst [82]. While in a Ru/C-A_2O_3 catalytic gasification of lignin process, the catalyst held low stability because of the change in its structure from gamma- to alpha-phase and the dissolution of active ruthenium species into SCW [91]. In addition, poisoning of noble metal catalyst active sites was reported in sulfur contained lignin supercritical gasification, sulfur poisoned the active sites for carbon–carbon bond breaking and the methanation reaction [92]. Sulfur is an inevitable component in most kinds of lignins, the deactivation effects of sulfur indicate that desulfurization is important in catalytic hydrothermal gasification of lignin.

Alkali and alkali salts drove to water–gas shift reaction, which subsequently turned to hydrogen and carbon dioxide production. And the effect of KOH on the water–gas shift reaction was more than that on metal nickel catalyst [78]. Alkali can neutralize organic acid in hydrothermal conditions, which should be in favor of improving the degree of lignin decomposition. In the gasification of lignin model compound pyrocatechol with the present of KOH, the gas composition was very near the calculated equilibrium values [78]. Moreover, addition of NaOH accelerated the decomposition of phenol and reduced the generation of dimers in SCW oxidation [93], while phenol is a necessary lignin hydrothermal conversion process product. In an industrially integrated SCW gasification, the high alkali content in black liquor proved to be important for achieving high gas yields, rich in hydrogen and without carbon monoxide production [61]. There are some drawbacks in using the alkali catalysts. (1) It is difficult to recover and reuse the alkalis because they are homogeneous catalysts, and the outflow of alkalis would result in environmental problems and (2) the existence of alkalis would deepen the corrosion of reactor at high temperatures. Further studies of alkali catalyst seem necessary, one promising method maybe the development of low-corrosion property organic base catalysts and/or heterogeneous solid alkali catalysts.

4.4. Partial oxidation SCW gasification

Partial oxidation SCW gasification is considered as an effective technology to enhance the gasification efficiency. The effects of oxidant in partial oxidation SCW gasification of lignin are as follows [94]: (1) oxidant can help decompose compounds with phenolic structure to improve the gasification efficiency; (2) inhibition of char production by oxidation of the formaldehyde produced in lignin conversion. Oxidant can improve the gasification efficiency, and an appropriate addition of oxidant can improve the yield of hydrogen in certain reaction condition. Jin et al. [94] found the gasification efficiency of lignin with 0.4 equivalent ratio of oxidant could reach 3.1 times of that without oxidant. While the equivalent ratio equaled 0.1, the yield of hydrogen from lignin increased by 25.8% compared with that without oxidant [94]. In a flow reactor system, Yoshida and Oshima obtained a high gasification efficiency of glucose–lignin mixture solution based on carbon up to 96% at 400 °C with partial oxidation SCW gasification [95]. Catalysts are studied in the oxidation of lignin and its model compounds. It was found that partial oxidation with base catalyst in SCW could be applied for H_2 formation from lignin, due to enhancement of HCHO formation and, HCHO decomposition, and water gas shift reaction [86]. In a SCW oxidation of phenol (lignin derived intermediates) catalyzed by activated carbon, the mass transfer within the pores of the activated carbon catalyst limited the overall reaction rate [96]. Sodium carbonate was found an effective catalyst to enhance the SCW oxidation of 2-chlorophenol and phenol significantly, possibly by lowering the activation energy for both 2-chlorophenol and phenol [97]. The addition of NaOH to 2-chlorophenol and phenol SCW oxidation reduced the generation of these dimers, and promoted the dechlorination of 2-chlorophenol under SCW oxidation conditions [93]. However, oxidation and gasification are competing reactions, for low levels of oxygen, the steam reforming reaction is more important than oxidation; while the oxygen coefficient value is very high, much more water and CO_2 would be obtained because oxidation becomes predominant. On the other hand, a reactor scheme for high corrosion protection is proposed because that SCW oxidation would result in significant corrosion of reactor surface.

5. Hydrothermal liquefaction

Hydrothermal liquefaction is a thermo-chemical process for obtaining liquid product, often called bio-oil from biomass in the presence of water as a solvent at a medium-temperature, high-pressure [98,99]. Hydrothermal liquefaction has potential to create lower-oxygen oil than fast pyrolysis and other thermo-chemical methods, part of the oxygen exists in small organic compounds hydrolyzed by the raw materials would partition into the aqueous phase. During hydrothermal process, the oxygen content of the organic material is reduced from about 40% to between 10 and 15% [100].

5.1. Liquefaction products

Hydrothermal liquefaction of lignin and its model compounds were widely studied in recent years. The objects of hydrothermal liquefaction of lignin are mainly converted to bio-oils and/or phenolics. The lignin-derived products in methanol-soluble portion were shown to have more phenolic hydroxyl groups than lignin original wood [31]. The formation of many chemicals with intact phenolic functional groups indicates that lignin hydrolysis plays an important role during the decomposition reaction. Phenolic compounds such as phenol, o-cresol and catechol are important intermediates in the chemical industry, hydrothermal liquefaction is an efficient way of recovering these compounds. The relative concentration of phenolic compounds in the lignin-derived oil reached about 80% in hydrothermal liquefaction of organosolv lignin [101]. While more than half yields of phenolics in the oil products would be obtained by hydrothermal liquefaction of alkaline lignin [102]. Main phenolics, including 28.37 wt% of catechol, 7.53 wt% of phenol, 7.87 wt% of m,p-cresol and 3.80 wt% of o-cresol were obtained from methanol soluble fraction of lignin liquefaction products [103]. Zhang et al. hydrothermal treated of five types of lignin and biomass residues, the yields of liquid products in total products were between 32.6% and 90.2% [104]. These results indicate that the yields are dependent on the composition or structure of the raw materials. Based on these results, it can be pronounced that hydrothermal conversion of lignin could be a promising method to obtain phenolics. However, the pretreatment process of obtaining lignin from biomass is important for getting high phenolic yields. Organic acid are another important product from lignin hydrothermal liquefaction. The production of organic acid from lignin is owing to decomposition of the propyl

chain of the phenyl propane unit but not the aromatic moiety in lignin [105], whereas benzene structure is highly stable during hydrothermal liquefaction treatment.

Temperature and reaction time are important factors in affecting the products distribution and yield of lignin hydrothermal liquefaction. With an increase in the reaction time at the same conditions, higher molecular weight fractions decreased and the amount of lower molecular weight fractions increased [103]. While higher temperature resulted in more alkyl-substituted phenols and fewer methoxyl aromatic products [102]. Zhang et al. found that the final liquefaction temperature, the liquefaction time, and the heating rate were the main factors to influence the liquid yields by hydrothermal liquefaction of grassland perennials and its extracted lignin, and they indicated that the liquid yields was increased drastically as the heating rate increased [106].

5.2. Liquefaction of model compounds

Many lignin model compounds were used in the hydrothermal liquefaction to explore the liquefaction mechanism [31,107–109] and reaction kinetics [107–110]. β-O-4-type lignin model compound were found easily to be cleaved, whereas biphenyl-type compounds were highly stable during SCW treatment [31]. Dealkylation and rearrangement reactions were found in the hydrothermal conversion of lignin model compound 2-isopropylphenol [110]. Wahyudiono found that decomposition of guaiacol tended to produce catechol and phenol rather than o-cresol, and the phenolic bonds were not easily cleaved at high temperatures [107]. While in the conversion of catechol, phenol was the main product, phenol was a stable hydrolysis product which contained a single ring [108]. Moreover, char was found by hydrothermal conversion of these low molecular phenolic model compounds (catechol, guaiacol) [107–109], which indicates that char is an inevitable product in an uncatalyzed lignin hydrothermal reaction, because phenolics are the necessary products in lignin liquefaction. These model compounds' reaction pathway also suggests that some useful chemical intermediates might be recovered in an appropriate speed and selective manner by changing the hydrothermal conditions, e.g. temperature.

5.3. Application and separation

The use of lignin liquefaction products is studied mainly considering the present of abundant phenolics. These phenolics have particular properties which can be used for the synthesis of pharmaceutical products, for the production of adhesives, and for the synthesis of specialty polymers [111]. The obtained phenolic oils directly from liquefied lignin may be useful phenol substitutes for the production of green phenol–formaldehyde resins. Xu et al. proved that lignin derived phenolics had the potential to be used as a substitute of phenol in preparing novolac resins [112]. Lignin derived phenolic compounds were reported possessing significant antioxidant properties [113]. It was found that phenolic compounds produced from lignin fraction of sugarcane bagasse and olive tree pruning had antioxidant activity [114–116]. Kang et al. found that the liquid products of both black liquor lignin and lignosulfonate could be used as antioxidants, and the antioxidants abilities had certain relationships with the total phenol content in the liquid products [117]. Besides the monomeric phenolics, dimeric phenolics were found in the lignin liquefaction products [118], while the dimeric phenolic compounds were examined having significantly higher antioxidants properties than that of monomeric phenolics [119]. Lignin liquefaction products can be used to improve the antioxidant abilities of biodiesel, and antioxidant biodiesel was produced in supercritical methanol with the addition of lignin [120]. However, some other nonphenolic compounds, e.g. carboxylic acids and alcohols, exist in the lignin liquefaction products. These nonphenolic compounds would modify the brittleness and increase the flexibility of the resins produced with the lignin derived liquids. In addition, the hydroxyl groups in the nonphenolic compounds would affect the antioxidant activity because their polar groups can hydrogen bond with lignin phenolic groups. Some interesting and valuable work has been reported to separate phenolic compounds from the organic acids, alcohols, and other components in lignin liquefied products. Kang et al. successfully separated the lignin liquefaction products into four types of substances: benzenediols, monophenolic hydroxyl products, weak-polar products, and water-soluble products (low-molecular-weight organic acids, alcohols, etc.) by using successive extractions with alkali solutions and organic solvent [102]. Molecular distillation is an effective method in the separation of bio-oil [121], which should be a promising method to recover phenolics from lignin liquefaction products. Several other methods, such as silica gel column chromatography [122], liquid–liquid extraction [111], also have potential to separate and obtain phenol-rich fractions.

5.4. Catalysts

The catalyst types in hydrothermal liquefaction of lignin are similar to that of gasification. Alkali, alkali salt and noble metal are the common catalysts. Sulfuric acid can be used as a catalyst, however, it was reported that lignin degradation reactions were activated thermally but were not effectively catalyzed by aqueous acid [123]. Hepditch and Thring investigated the effects of lewis acid catalysts in producing liquid products from lignin, they found that lewis acid catalysts $FeCl_3$ clearly favored the production of catechol, whilst syringol and guaiacol were the major compounds obtained from $NiCl_2$, however, both catalysts could not effectively degrade the lignin, but apparently favor condensation reactions leading to the formation of insoluble residue [124]. In the hydrothermal liquefaction of lignin in empty palm fruit bunch, the reactivity of the alkalis was in the order of $K_2CO_3 > KOH > NaOH$, and it was found that lignin degradation was quite sensitive to K_2CO_3 concentrations, higher K_2CO_3 catalyst concentrations supported re-polymerization which resulted in sharp decrease in lignin degradations [125]. Yan et al. found that Pd/C catalyst could cleave the C–O bonds without disrupting the C–C linkages in lignin [126], yielding four main monomers, namely guaiacylpropane, syringylpropane, guaiacylpropanol, and syringylpropanol.

The ideal object of the catalysts in hydrothermal liquefaction of lignin is to cleave the bond among lignin's three phenolic structural units and to inhibit the condensation, without decomposing the benzene ring structure. Further research on development of high performance catalysts seems necessary.

Table 2
The supercritical points of alcohols and organic acids.

Substances	Water	Methanol	Ethanol	Acetic acid	Formic acid
Critical point	374.1 °C, 22.1 MPa	239.4 °C, 8.1 MPa	240.7 °C, 6.4 MPa	320 °C, 5.8 MPa	306.8 °C, 8.6 MPa

6. Hot-compressed organic solvent–water solution conversion

Decomposition of lignin in hot organic solvent–water solution was reported by some researchers, these organic solvent mainly include low molecular weight organic acids, alcohols, and phenolics. The presence of organic solvents owns some obvious advantages, the first obvious advantage of organic solvent is that it improves the solubility of lignin and its decomposition products; while in SCW at temperature of 400 °C, little of lignin was dissolved, and no homogeneous phase was found for the (lignin+water) system [127]. Second, some organic alcohol and acid solvents, such as methanol, own a low critical point of the supercritical condition, as shown in Table 2. There is a possibility that the value of reaction temperature and/or pressure of decomposition of lignin can be decreased by the presence of alcohols or organic acids. Moreover, methanol can be used as a hydrogen donor in lignin liquefaction, which was in favor of low oxygen content oils production [128].

In supercritical water and phenol mixtures, lignin can be completely dissolved and undergone homogeneous hydrolysis and pyrolysis that prevents further re-polymerization [127]. No char formation was found when phenol was used in SCW conversion of lignin, there were mainly two reasons [127,129]: firstly, char formation was depressed due to entrapment of active fragments and capping of active sites occured by excess phenol; secondly, addition of phenol promoted de-polymerization of lignin by hydrolysis in a homogeneous phase and its re-polymerization by phenol was most likely inhibited. In the presence of phenol, Saisu et al. found the molecular weight distribution of lignin liquid products shifted toward lower molecular weights than those in the absence of phenol, and some alkylphenols were obtained only in the presence of phenols, because of the reaction of phenol with the decomposition products [130]. Matsumura et al. found that addition of p-cresol for lignin conversion in water was also an effective method for conversion of lignin to lower molecular weight fragments, and they indicated that other alkyl phenols with vacant ortho or para positions of hydroxyl groups could also be used as capping agents [131]. Kleinert and Barth found that lignin could be thermal converted into a liquid bio-oil with very low oxygen content, high liquid yields and H/C ratios, when using formic acid or an alcohol as cosolvent [132]. Xu et al. found that in an alkali catalytic supercritical methanol solution, lignin conversion based on carbon was up to 93. 53% with the yield of total oil 94.96%, and lignin can be completely decomposed within the reaction time of 10 min [133,134]. Aqueous methanol was also an effective solution for oxidation of lignin for production of aromatic aldehydes and aromatic esters, the extracted liquid products containing vanillin (3.5 wt%) and methyl vanillate (3.5 wt%) with a yield of 65 wt% were obtained by oxidation of industrial kraft lignin in aqueous methanol [42].

In conclusion, the use of organic solvent would decompose lignin in a relative mild reaction conditions with the inhibition of char formation. The present of phenol in hydrothermal condition is ponderable for phenolics production from lignin; while the present of alcohol is value for low oxygen content lignin derived oils production. However, the use of the organic solvent could yield some problems, for example, a high cost of the solvent should be considered; the application and recycling of a large quantity of organic solvent (such as phenol or methanol) may result in some environmental problems.

7. Lignin hydrochar

The hydrochar seems an inevitable product in lignin hydrothermal conversion, which mainly consists of unconverted lignin and lignin derived high molecular polymers. Hydrochar is usually considered as an undesirable product no matter in lignin hydrothermal gasification or liquefaction. There are mainly four disadvantages of the existence of hydrochar. (1) A high yield of hydrochar means a low yield of liquid and/or gas yield, which is unfavorable for the conversion of lignin, (2) in a catalytic reaction, hydrochar formation in catalyst surface would result in an irreversible deactivation of the catalyst by decreasing of specific surface area and losing of active sites, (3) existence of hydrochar would lead to the block of the reactor or pipe in a continuous reactor and (4) covering of the raw material lignin with the hydrochar would result in an inhibition of further conversions, such as hydrolysis reaction.

Some mechanisms on lignin hydrochar formation are discussed. At high temperatures, a phenolic char can be formed via homogeneous polymerization of the phenolics and water-soluble compounds; on the other hand, non-dissolved lignin underwent heterogeneous pyrolysis and formed polyaromatic char [127,135]. Furthermore, the existence of formaldehyde during lignin hydrothermal conversion would result in high hydrochar yield, which promote the polymeric phenolic hydrochar formation [136]. Besides, higher temperature and reaction time led to polymerization and carbonization of monophenols, which resulted in high yields of char [137,138].

8. Effects of lignin in biomass hydrothermal conversion

Lignin is thermally more stable than the other biomass, and the order of hydrothermal conversion degree of biomass and biomass component was as follows: cellulose > sawdust > rice husk > lignin [139]. In the liquefaction of switchgrass in subcritical water, the residue solid mainly contained lignin fractions [27,28]. The soft wood biomass contains higher lignin content than hard wood biomass, it was reported the lignin rich cypress (soft wood biomass) produced the hydrocarbons with major portion of phenolic hydrocarbons and derivatives than cherry (hard wood biomass); while the formation of acetic acid was more in the hemicellulose and cellulose rich cherry than cypress [140]. Compared with the cellulose, lignin is hard to gasify. Only 30% of gas yields were obtained in lignin SCW gasification at 400 °C with a ruthenium catalyst; while 70% of gas yields were obtained in gasification of cellulose in the same conditions [63]. In the hydrothermal conversion of the mixtures from different ratio of cellulose to lignin, the char yields increased with the increasing lignin content, and the yields of gas and aqueous soluble products increased with the increasing cellulose content, but it was difficult to conclude the oil yields change with increasing lignin content [141]. Cellulose and lignin mixture was gasified with a nickel catalyst in SCW at 400 °C, lignin was found interacted with cellulose, retarding its gasification; and nickel catalysts were deactivated from the reaction between cellulose and lignin [142]. Moreover, different lignin reagents showed different gasification characteristics, mixtures of cellulose with hardwood and grass lignin were gasified much more easily than the mixture of cellulose with softwood lignin [142]. It was reported that cellulose or xylan was likely to function as a hydrogen donor to lignin [143,144], which resulted in a decrease in gas yield and H_2 production by gasification of cellulose, xylan, and lignin mixtures in SCW. Weiss-Hortala et al. found that phenol (substitute for lignin) reduced hydrogen yield and particularly the total volume of gas from the conversion of glucose (substitute for cellulose), they indicated that one possible explanation was that phenol worked as a free radical scavenger [145]. The phenolics also inhibited the oxidation of cellulose under hydrothermal condition, and this inhibition was reported related closer to the stability of phenolic compounds under oxidation conditions rather than the ease to

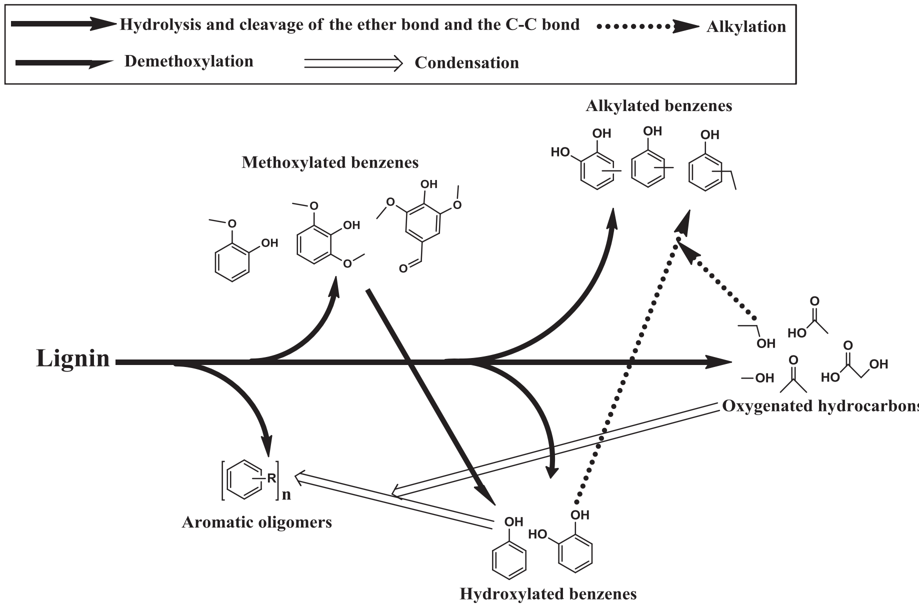


Fig. 3. Proposed mechanism of lignin hydrothermal liquefaction [102,150].

remove phenolic hydrogen on the OH group [146]. On the other hand, gasification of a mixture of hemicellulose and lignin by SCW may promote the conversion of lignin by facilitating hydrogenation, using H_2 generated by rapid reforming of hemicellulose [147]. It was reported that the cost of biomass SCW gasification product gas was very high, which was 1.86 times more expensive than city gas in Tokyo in 2002 [148], while lignin is probably the most difficult decomposition constituent in biomass SCW gasification for gases production, therefore improving the gasification efficiency of lignin can be a key technology to decrease the cost of product gas.

A set of equations can be used to estimate the amount and composition of the product gas accurately predicted the actual results using only the lignin fraction as a parameter [143]. However, Madenoglu et al. found that a relationship between the lignin content of the feed and the product yield and the composition of the product gas was not distinguishable for five selected biomass samples [149], this may be due to the differences in the structure and composition of lignin in the different feeds. In conclusion, more char and lower gas yields would be obtained in hydrothermal conversion of carbohydrates with the presence of lignin. However, further investigation is needed in order to predict which biomass is more suitable to get gas products by considering its lignin content and structure. Moreover, further investigation to improve the conversion of lignin seems necessary for getting fuel and low molecular weight chemical products from raw biomass.

9. Mechanism of Hydrothermal gasification, liquefaction, and wet oxidation

As shown in Fig. 3, in the hydrothermal liquefaction of lignin for phenolic production, hydrolysis and cleavage of the ether bond and the C–C bond, demethoxylation, alkylation and condensation reactions were occurred [102,150], and those main reactions happened to be in competition [150]. Cleavage of the $\beta-O-4$ ether bond was reported had the precedence in the decomposition of lignin and its model compounds [31,151,152,153], C_α–C_β was also an easy-broken bond [151]. On the other side, the aromatic rings are generally not affected by hydrothermal reactions [150], and the biphenyl-type compounds were highly stable during SCW treatment [31]. These indicate that phenolic monomers and

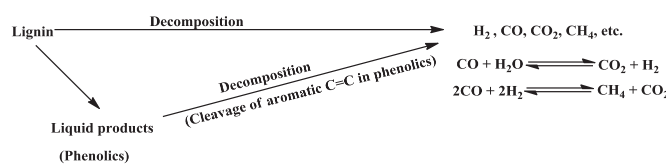


Fig. 4. Reaction routes of lignin hydrothermal gasification.

dimers could be obtained by preliminary cleavage of ether bond and aliphatic C–C bond in a mild condition of relative low temperature and short reaction time. The demethoxylation and alkylation of lignin derived phenolic compounds would be enhanced as the temperature increased [102], so various alkyl phenols could be obtained at high temperature. Besides, Lin et al. found in the lignin liquefaction, the reaction intermediates with aliphatic side chains showed large reactivity and, therefore, they further condensed with phenol or with each other to convert into the multi-condensed product [154].

In the liquefaction, the formation of many phenolics indicates that lignin fragmentation reaction is not played a main role during the decomposition reaction of lignin structure. On the contrary, fragmentation is a vitally necessary reaction pathway in the lignin hydrothermal gasification. Lignin gasification in SCW is a complex process, which includes a group of successive reactions and competing intermediate reactions, including hydrolysis, monomer oligomerization, monomer decomposition, steam reforming, char formation through intermediates, water–gas shift, methanation, hydrogenation, pyrolysis, and hydrogasification [85]. As shown in Fig. 4, the hydrothermal gasification of lignin mainly consists of three steps [81,85,89]: (1) decomposition of lignin into lower-molecular weight liquid products, just abs the liquefaction step; (2) fragmentation of the lower-molecular weight liquid products for gas production, including cleavage of aromatic C=C in phenolic compounds; (3) gas species react between themselves, such as water–gas shift, methanation reaction. During the third step, the total gas yield should remain roughly constant, but the product distribution would be changed. CH_4 was probably derived from both the methanation reactions and the dealkylation of alkyl groups on alkylphenol structures in the lignin [63]. While the hydrogen can be produced from direct depolymerization of lignin, besides some hydrogen should be obtained from water by water–gas shift and steam reforming reactions. In the gasification of biocrude, the maximum

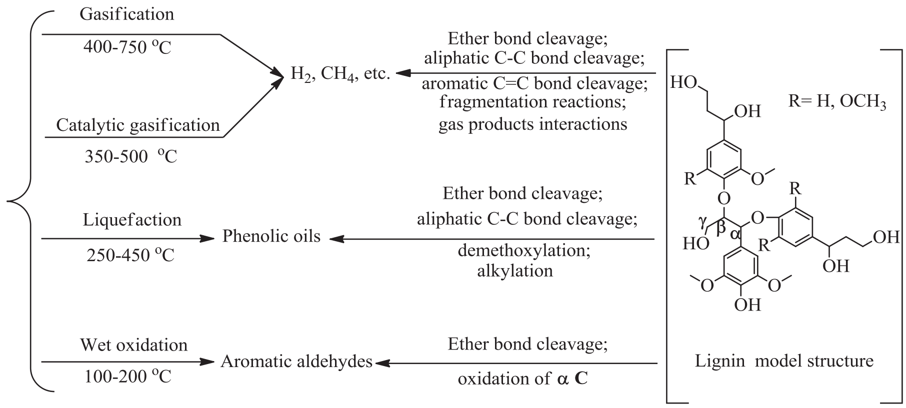


Fig. 5. The temperature ranges and reactions of lignin hydrothermal conversion.

theoretical hydrogen yield would be attained approximately 2 mol H_2/mol C [155]. Phenolics are found to be rather inert with regard to gasification, and certain works have been done for the gasification of phenolics in SCW. Some alkylphenols acting as lignin derived preliminary decomposition products were gasified in SCW with supported noble metal catalysts, it was found that dehydroxylation occurred easier than dealkylation, and the reactivities of o- and p-alkylphenols were relatively higher than those of m-alkylphenol [90].

In the wet oxidation of lignin, the aromatic aldehydes can be produced by cleavage of ether bond and appropriate oxidation of the α C in the phenylpropane. Vavious mechanisms were supposed. Deng et al. proposed mechanism of the wet oxidation of lignin in the catalytic and noncatalytic process, quinonemethide and hydroperoxide were supposed as intermediates, and the formation rates of the intermediates were the rate-determining steps [37,38]. Sales et al. indicated that the lignin precursors were depolymerized in an oxidant media with a dialcohol formation, whose C–C bond was then submitted to an oxidative splitting [42]. These produced aldehydes may, in a further oxidation, be transformed to their corresponding acids. Tarabanko et al. proposed that lignin oxidation to vanillin process began with the formation of a phenoxyl radical and ended with the step of retro-aldol cleavage of substituted coniferaldehyde to vanillin [54].

Comparing these three hydrothermal methods, higher temperature is required for gasification. One of the reasons is that higher temperature favoring complete gasification of the phenolic compounds. While a relative low temperature (< 200 °C) is required for wet oxidation, because that high temperature would favor the over-oxidation of lignin to form aromatic acids instead of aromatic aldehydes. The temperature ranges and reactions of these three kinds of lignin hydrothermal conversion are summarized, as shown in Fig. 5.

10. Summary

As a renewable and abundant natural resource, the utilization of lignin has become a research hotspot. Hydrothermal technology is an attractive and promising method for lignin conversion owing to its unique nature and the sound environmental compatibility. There are mainly three categories in utilizing lignin by hydrothermal method: wet oxidation, liquefaction, and gasification. Both wet oxidation and hydrothermal liquefaction are to break up lignin's macromolecular structure but maintain the nature aromatic building units, the objects are to get aromatic aldehydes and phenolics, respectively. In the hydrothermal gasification, lignin is used as a carbon-rich source, the object is to fragmentate lignin' polymeric structure to form fuel gases.

Hot-compressed organic solvent–water solution conversion of lignin is benefit to get liquid products. However, cost reduction, recovery, and reuse of the solvent are urgent problems to be solved. The hydrothermal gasification of lignin for fuel gas production is not a favorable method because of its required high temperature and low gasification efficiency. However, it is necessary to improve lignin gasification technology, which is helpful to get fuel gas from the whole biomass by hydrothermal method. Wet oxidation of lignin has apparent advantages due to its required relative low temperature, and vanillin production form lignin has been in industrialization. The required hydrothermal liquefaction temperature is not harsh, and phenolic compounds are valuable chemical intermediates, hydrothermal liquefaction would be a promising method for exploitation of lignin.

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